Limitations of Existing Analytical Methodologies-
Needs for Future Methods Development in The Analysis
of Fossil Fuels: Concluding Remarks

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## Introduction

Two of the challenges faced by fuel scientists with respect to a future fuel-processing technology are (1) the need to characterize highly complex samples in various stages of conversion, and (2) the need to aid in developing conversion processes that are economically feasible and yield a product that is environmentally acceptable. The Committee on Nuclear and Alternative Energy Systems concludes that coal and nuclear energy are the only potential major sources for electricity generation in this century.[1] For this reason, and since most of the papers in this symposium have been directed toward investigations relevant to coal, this discussion will focus on problems associated with the characterization of coal and its concomitant processing products.

An understanding of coal requires integration of the perspectives of investigators from various backgrounds. For example, even today there is still no concensus concerning the origins of the various forms of sulfur in coal that integrates the views held by scientists from different disciplines. Socolow[2] noted the various views of coal from miners, geologists, chemists, and biologists. Today, this list can be expanded to include views of coal from social scientists and environmentalists. Socolow quotes the noted geologist David White, who once said, "Coal is like character, the deeper you go into it, the more interesting it becomes." Thus, to a great extent each investigator becomes more or less captivated by these materials and the analytical challenges they offer, such that if the muse of fuel science were to appear to each of us and offer one gift of instrumentation, we would each of us request a different gift, the final assemblage of which would require standardization and cross calibration.

In the absence of a muse, it might be interesting to trace the stages of evolution of a new analytical method. Laitinen[3] has described a set of seven phases through which an analytical method passes. The phases he describes are traced in terms of the history of infrared spectroscopy and can be summarized as follows:

> First, there is a conception phase that occurs after a principle of physics (e.g., the absorption of infrared radiation) is recognized as a basis for identification and measurement. Second, the validity of the principle as a basis for useful measurements is established. Third, instrumental developments bring the method from a laboratory curiosity into the hands of a nonspecialist. Fourth, detailed studies of principles and mechanisms are pursued, and the method matures as an accepted procedure. (Laitinen identifies this stage as the crest of analytical research as distinguished from instrumentation research). Fifth, applications are enlarged with appropriate modifications in procedures. Sixth, well-established procedures are applied to new as well

as to old problems. Seventh, a period of senescence occurs while other developing methods surpass the method under consideration. Finally, a resurgence of these later phases may occur as new developments in instrumentation or theory come along.

Two questions come to mind in considering these stages of evolution of accepted analytical methodology: First, has physics recognized new principles that suggest new methods for probing fossil fuels; and second, are fuel scientists actively developing methods applicable to these materials or are we merely modifying methods that were originally developed for investigation of other sample types (i.e., polymers, proteins, amino acids, biological materials)?

"It has been said, perhaps cynically, that chemists can expect to see no further new analytical methods. Physicists have discovered the fundamental interactions of energy and matter, and combining existing techniques into hyphenated methods is all that remains."[4] Is it reasonable to expect the development of new analytical methods for the analysis of fossil fuels? A historical view of coal utilization might produce some insights.

Past, Present, Future Trends

Some well-established laboratory techniques for the analyses of coal and petroleum have been identified and are accepted by the American Society for Testing and Materials (ASTM) as standard methods. There are, however, three other organizations that specify methods and procedures for coal analysis, including (1) International Organization for Standardization (ISO), (2) Deutsches Institut für Normung (DIN), and (3) British Standards Institution (BSI). Procedures recommended by these four standard-setting groups were compared at Conoco's Coal Research Division (Library, Pa.) using an Eastern United States high-sulfur coal.[14] They note that although the terms used by these different standard setting groups are the same, the procedures used for some of the determinations are not, and results obtained from these analyses show that differences exist. Finally, they conclude that "the increasing movement of coals from the U.S. or other parts of the world to Europe requires an understanding of the various methods of coal analysis used by coal buyers and sellers." Thus, a fundamental problem is confirmed that must be addressed by investigators of fossil fuels, the necessity for methods calibrations and standardizations.

Coal preparation (beneficiation) can be viewed as a form of coal processing that should be well understood. Coal prep has been used in the U.S. for approximately 100 years. In the 1960s, about 1/3 of the total coal mined was cleaned. As Klatt has pointed out,[5] coal prep and flue gas desulfurization are the least costly ways of meeting New Source Performance Standards for $SO_2$ emissions.[6,7] Yet, the application of analytical methodologies to the characterization of these materials and processes have been minimal. Klatt cites several reasons for this deficiency;[5] he points out that fundamentally coal is undervalued relative to other fuels, and the coal industry has been reluctant to try new technology. As evidence of this observation, Klatt relates the cost of a modern coal prep plant is approximately $75,000,000, with a total on-line instrumentation cost of about $150,000 -- a much lower investment in instrumentation than is found in the chemical industry. The economic rationale for the use of on-line process and quality control instrumentation, Klatt notes, has simply not been provided. Most laboratory techniques used to analyze coal cannot be transferred to on-line instruments because they do not satisfy principle design criteria (i.e., rapid response time and the ability to sample large quantities of materials). Other important criteria that must be considered include cost, reliability, and maintainability. Methods that use high-energy photons, gamma or X-ray, can meet the above design criteria. Consequently, essentially all systems developed or under development (i.e., Mossbauer spectroscopy, X-ray diffraction, and X-ray fluorescence) for the coal industry that yield elemental composition information employ methodology involving the measurement of gamma or X-rays.

The assessment of the mechanisms, efficiency, environmental acceptability, etc., of a particular processing technology may require knowledge of the functionalities present or a determination of the individual organic compounds present. Hertz et al.[8] have briefly reviewed emerging methods for the analysis of individual organic compounds in petroleum, shale oil, and synthetic coal liquids. However, they note that none of these methods was developed for the accurate quantitative analysis of individual compounds. Because of sample solubility or volatility requirements, in many cases, the actual sample for which data are reported is a fraction or derivative of the material of interest that has been subjected to a variety of pretreatment procedures. Because of their carcinogenic potential and because they are present at significant levels in combustion products, polycyclic aromatic hydrocarbons and their heterocyclic analogue derivatives have been the focus of many recent investigations. Analytical methods that have been applied to the analysis of these sample constituents have been reviewed.[9,10,11] Karasek et al.[12] and Janardan and Schaeffer[13] have reviewed the mechanisms involved in the introduction of errors in the analysis of trace organics. Karasek et al. address problems associated with solvent purity, sample preconcentration, and sample collection and handling; they suggest that a major problem with all techniques for trace analysis of organics is the lack of appropriate environmental standards.[12] They recommend specific changes in the design and use of glassware and other apparatus employed in sample preparation. Likewise, in an analysis of random errors in estimating levels of trace oganics in environmental sources, Janardan and Schaeffer[13] show that the estimated quantity is dependent on the capture efficiency and precision, the average recovery and reproducibility, and the sensitivity of the analysis. They concluded that "in order to insure the accuracy of such data, the scientist must control not only the analyses but, more importantly, the processes involved in obtaining the sample itself."[13]

Many of the future needs in fossil energy research are fundamental to the ordinary requirements for the analysis of any diverse complex sample type. There must be developed a series of suitable, universally acceptable standards that are appropriate for instrumental and methods calibration for routine analyses. Intermethod and intramethod calibration is vital if results and conclusions from the investigations of the various fossil fuel types are to be compared and contrasted. These tasks will require the expertise and background of the most reputable and credible fossil fuels scientists among us if their results and suggestions are to be widely accepted and implemented. This endeavor would be unique in that the study would attract the worldwide interest and support of fossil fuels scientists. Finally, the translation of these laboratory methods into a form suitable for on-line process analyses with the appropriate cross-calibration and cross-validation of results should be forthcoming.

## New Methods for Fossil Fuels?

Who will accept the risks and bear the costs of new analytical methods development in fossil fuels research? Few young investigators can accept a high risk of failure; certainly graduate students and nontenured professors have timetables that are relatively intolerant of failure. However, significant contributions have been made and should continue in incremental improvements in existing methodologies applied to fossil fuels; these investigations can be accomplished, in many cases, within a time frame and within a risk factor acceptable to the new researcher. The fresh approach and ideas of new investigators should be brought to bear on fundamental problems of fossil fuels research. Federal budgets are being increasingly scrutinized, and the requisite for fossil fuels development is being delayed. Increasingly, managers outside of academia are adopting the "publish-or-perish" criterion for promotion or even retention of entry level professionals. A conference, "Strategies for Innovation," sponsored by an international accounting firm, convened in London in June 1985.[15] There Douglas Dybvig, managing director of Minnesota 3M Research, Ltd., pointed out that "the rising cost of innovation, pressures from investors for immediate gains, and economic pressures have helped reduce productive growth and concomitant growth in innovation." Two primary themes emerged from the conference. One was the need for companies to establish an atmosphere in which people are not afraid to fail; the second was the need for companies to be accepting of not only in-house ideas but also those from the outside. Without significant changes in this philosophy and these attitudes, it is reasonable to conclude that the risks of failure associated with new methods development will probably be the burden of established professionals -- established professionals who must consciously purge old biases and precepts, and bring a youthful approach to problems, established professionals who have secure and adequate budgets to staff their laboratories with capable personnel willing to endure the painstaking, slow, and patient approaches required of innovation and creativity.

References Cited


1. Brooks, H., Proc. Am. Philos. Soc., 125, 245 (1981).

2. Socolow, A.A., "Coal in Pennsylvania," Educational Series No. 7, Commonwealth of Pennsylvania, Department of Environmental Resources, Bureau of Topography and Geologic Survey, 1968.

3. Laitinen, H.A., Anal. Chem. 45, 2305 (1973).

4. Stinson, Stephen, C., C&EN 63, 21-32 (November 11, 1985).

5. Klatt, L.N., Analytical Instruments in the Coal Preparation Industry - Current Status and Development Needs, in "Coal and Coal Products: Analytical Characterization Techniques," E.L. Fuller, Jr., ed., ACS Symposium Series 205, American Chemical Society, Washington, D.C., 259-279, 1982.

6. "Engineering/Economic Analysis of Coal Preparation with $SO_2$ Cleanup Processes," EPA-600/7-78-002, U.S. Department of Energy, Pittsburgh, Pa., 1979.

7. "Environmental Assessment of Coal Cleaning Processes: Technology Overview," EPA-600/7-79-073e, U.S. Environmental Protection Agency, 1979.

8. Hertz, H.S., Brown, J.M., Chesler, S.N., Guenther, F.R., Hilpert, L.R., May, W.E., Parris, R.M., and Wise, S.A., Anal. Chem. 52, 1650-1657 (1980).

9. White, C.M., Determination of Polycyclic Aromatic Hydrocarbons in Coal and Coal-Derived Materials, in "Handbook of Polycyclic Aromatic Hydrocarbons," Alf Bjørseth, ed., Marcel Dekker, Inc., 1983, 525-616.

10. Lee, M.L., Novotny, M.V., and Bartle, K.D., "Analytical Chemistry of Polycyclic Aromatic Hydrocarbons," Academic Press, New York, N.Y., 1981.

11. Hurtubise, R.J., "Solid Surface Luminescence Analysis - Theory, Instrumentation, Applications," Marcel Dekker, Inc., New York, N.Y.

12. Karasek, F.W., Clement, R.E., and Sweetman, J.A., Anal. Chem., 53, 1050A (1981).

13. Janardan, K.G., and Schaeffer, D.J., Anal. Chem., 51, 1024 (1979).

14. "Comparison of ASTM, ISO, DIN, and BSI Methods of Coal Analysis," Technical Bulletin (TB-4 9/83 ELO), Coal Research Division, Conoco, Inc., Library, PA 15129.

15. C&EN, 63, 16 (July 1985).